

# 8 Microstructure and transport properties of concrete

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## 8.1 Introduction

Concrete is a composite material whose microstructure is random over a wide range of length scales. At the largest length scale, concrete can be considered to be a mortar-rock composite, where the randomness in the structure is on the order of centimetres, the size of a typical coarse aggregate. Mortar itself can be considered to be a cement paste-sand composite, with random structure on the order of millimetres. Cement paste can also be considered to be a random composite material, made up of unreacted cement, CSH, CH, capillary pores, and other chemical phases. The randomness in the cement paste microstructure is on the order of micrometres. Finally, CSH is itself a complex material, with random structure, as seen by neutron scattering [8.1], on the order of nanometres. This range of random structure, from nanometres (CSH) to centimetres (concrete) covers seven orders of magnitude in size! It is a large and difficult task to try to relate microstructure and properties theoretically for concrete. However, there are some simple, basic ideas that do provide a framework for this task, with the main difficulty being carrying these ideas through to specific application.

This chapter attempts to outline the general principles that must be considered in trying to understand microstructure transport property relationships in concrete, or indeed any other random porous material. Specific applications to cement paste, mortar, and concrete will be considered. An earlier review [8.2], which mentions some of the ideas discussed in this chapter, is also a helpful reference for some of the earlier transport property data and their interpretation in terms of pore structure.

## 8.2 Basic concepts

Typical transport processes important in concrete are transport of water under a hydrostatic pressure head, transport of water by capillary suction,

the diffusion of ions under an applied concentration gradient, and the transport of ions by moving water. For these kinds of properties, two very simple ideas control how the spatial geometry of the microstructure affects transport properties. These ideas can be expressed in terms of **tube theory**: (1) large-diameter tubes have higher transport rates than small-diameter tubes, and (2) tubes that are blocked have zero transport rates. These ideas, phrased more rigorously as **pore size** and **connectivity**, provide the theoretical framework necessary for describing how the transport properties of concrete depend on pore structure. The idea of connectivity will be discussed first.

### 8.3 Description of connectivity by percolation theory

The ideas of percolation theory are very helpful in understanding the important features of random structures. The main concept of percolation theory is the idea of **connectivity**. Picture some sort of structure being built up inside a box by randomly attaching small pieces to a pre-existing central core. Percolation theory attempts to answer the question: at what point does the structure span the box? An alternative form of this question, for a random structure that already spans the box, is: if pieces of the structure are removed at random, when will it fall apart? The **percolation threshold** is defined by the value of some parameter, say volume fraction, right at the point where the structure either achieves or loses continuity across the box.

Figure 8.1 shows a simple two-dimensional example of these ideas. Circular blobs of 'paint' are thrown down at random on a clean sheet of paper, and the area fraction covered by the paint is monitored until the paint blobs form a continuous structure. It is found numerically that the paint blobs will become continuous when they cover approximately 68% of the paper [8.3]. In Fig. 8.1 the circles have an area fraction of 72% and so form a connected path. This is an example of the percolation of a structure that is being randomly built up. If we now think of the paper as a conducting sheet, and the paint blobs as circular holes that are randomly punched out, then the sheet will lose connectivity and its ability to carry an electrical current at an area fraction of 32%. This is an example of the percolation of a structure that is being randomly torn down. Concrete exhibits both kinds of percolation processes, as discussed further below.

### 8.4 Pore size effects on transport properties

As was stated in the introduction, it is obvious that the wider the tube carrying the flow, the greater the flow will be. One addition to this obvious

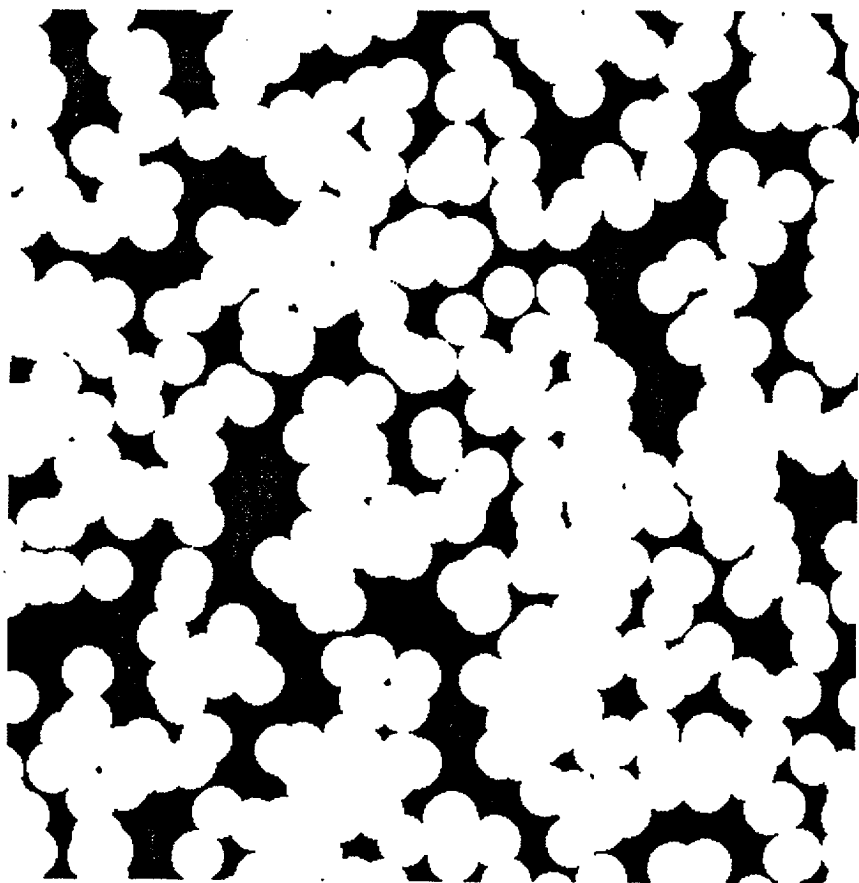


Fig. 8.1. Showing a unit cell of a system of randomly centred monosize circles, where 72% of the area is covered by the circles. The circles form a continuous phase.

notion, however, is that the tube or pore size will affect different transport properties in different ways. For example, consider an  $L \times L \times L$  cube of porous material, where the pore space is in the shape of a single tube of radius  $R$ , as in Fig. 8.2(a). The transport properties of such a simple material are easy to compute. The porosity is  $\phi = \pi R^2/L^2$ , the permeability is  $k = \pi R^4/(8L^2)$  [8.4], and the ionic diffusivity, if the pore is filled with a fluid in which the ions of interest have an intrinsic diffusivity  $D_o$ , is  $D = D_o \pi R^2/L^2$ . Figure 8.2(b) shows an  $L \times L \times L$  cube of another material whose pores are in the shape of  $N$  ( $N = 4$  in the figure) parallel tubes of radius  $r = R/N$ . The porosity is the same, since in this case  $\phi = N(\pi r^2/L^2) = \pi R^2/L^2$ , but now there are more pores and they are smaller. The diffusivity will be unchanged as well, since  $D = D_o N(\pi r^2/L^2) =$

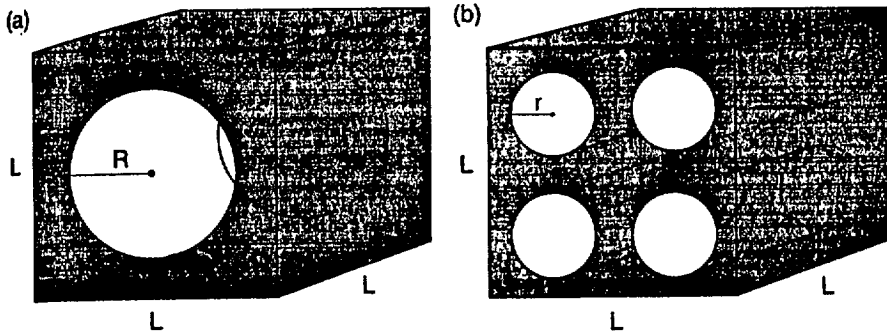


Fig. 8.2. Showing two simple models of a porous material, where the pores are straight, parallel tubes of uniform width passing through the solid material: (a) one tube of radius  $R$ , (b)  $N = 9$  tubes of radius  $r = R/\sqrt{N} = R/3$ .

$D_0 \pi R^2 / L^2$ . However, the permeability is now different and smaller, since  $k = N[\pi r^4 / (8L^2)] = (1/N)[\pi R^4 / (8L^2)]$ . This argument will be valid, in general, even for random pore structures, so that it is important to remember that fluid permeability and ionic diffusivity depend on pore size in different ways. They will depend on pore connectivity in a similar manner, however.

## 8.5 Cement paste

We now specifically consider the microstructure-transport property relationships in cement-based materials. It is important to begin with cement paste, as this is the matrix material that, along with sand and rock inclusions, forms the concrete composite. It is difficult to understand the behaviour of a composite without first understanding each constituent separately.

For simplicity, and because it still correctly captures the main features of the pore structure, cement paste can be thought of as consisting of four phases: (1) unreacted cement, (2) surface products like CSH, (3) pore products like CH, and (4) capillary pore space. Surface products grow out from the unreacted cement particles and contain continuous gel pores, while pore products are generally crystalline and fully dense, with no connected pores. The capillary pores are the left-over space between solid phases.

### 8.5.1 PORE CONNECTIVITY

Cement paste is itself a random porous material, with more than one distinct solid phase. Percolation ideas can be applied to each particular material phase, and the 'box' taken to be the macroscopic sample. The

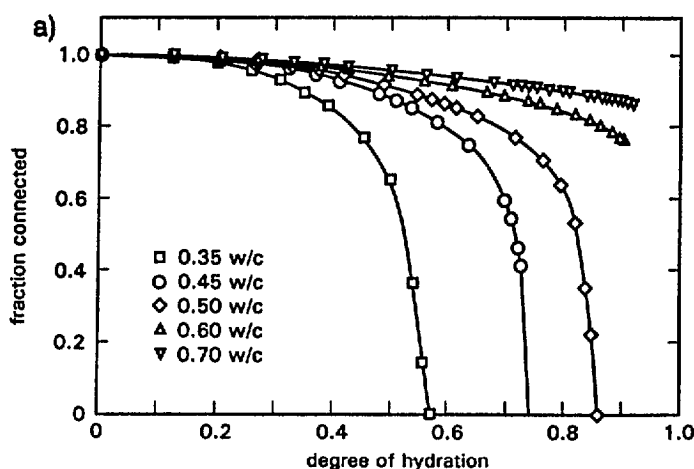
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connectivity of the different phases, and particularly the pore phases, changes with time.

Immediately after mixing, the solid phases are discontinuous, and so the freshly mixed paste is a viscous liquid. The solid phase is then built up through random growth of reaction products, and at some point becomes continuous across the sample, mainly due to the formation of the CSH surface products [8.5]. This percolation threshold is then a rigorous theoretical definition of the set point.

A percolation threshold that is more important for transport processes is the point at which the capillary pore space loses continuity. Such a percolation threshold can exist, because as hydration products are formed, pieces of the capillary pore space will be trapped and cut off from the main pore network, thus reducing the fraction of the pores that form a connected pathway for transport. As this process continues, the capillary pore space can lose all long-range connectivity, so that 'fast' transport of water or ions through the relatively large capillary pore system would end, and 'slow' transport would then be regulated by the smaller CSH gel pores.

Results from recent computer simulation work provide evidence for such a percolation threshold. Figure 8.3(a) shows the 'fraction connected' of the capillary pore space vs degree of hydration for several water/cement ratios, as computed by a computer simulation model of cement paste microstructure [8.6]. The quantity 'fraction connected' is defined as the volume fraction of capillary pores that make up a connected path through



**Fig. 8.3.** Showing the fraction of the capillary pore space that is part of a percolated (continuous) cluster, for several different water/cement ratio cement pastes as a function of: (a) degree of hydration, and (b) capillary porosity.

the sample, divided by the total volume fraction of capillary pores. Immediately after mixing, the cement particles are totally isolated, assuming adequate dispersion, and so the connected fraction of the capillary pore space is 1. As hydration occurs the connected fraction decreases gradually. If continuity is lost at some critical degree of hydration, the 'fraction connected' will go to zero. Such a percolation threshold can be seen in all the water/cement ratios plotted, except for 0.6 and 0.7. We have found in the model that water/cement ratios of 0.6 and above always have a continuous (or percolated) capillary pore system. This prediction is in good agreement with experiment [8.7]. It is clearly seen in Fig. 8.3(a) that as the water/cement ratio decreases below 0.6, less and less hydration is required to close off the capillary pore system.

In order to unify the previous results, we have replotted all the data from Fig. 8.3(a) in Fig. 8.3(b) against capillary porosity. All the connectivity data now fall on one curve, and it is clearly seen that there is a common percolation threshold at a critical value of capillary porosity of about 0.18. Even the 0.6 and 0.7 water/cement ratio data fall on this curve, and now it is clear why these pastes always have an open capillary pore space: there is not enough cement present originally to be able to bring the capillary porosity down to the critical value, even after full hydration. The capillary pore space percolation threshold for cement paste will have some sensitivity to cement particle size distribution and degree of dispersion, so that the critical value of capillary porosity for percolation should be considered to be about  $18 \pm 5\%$ .

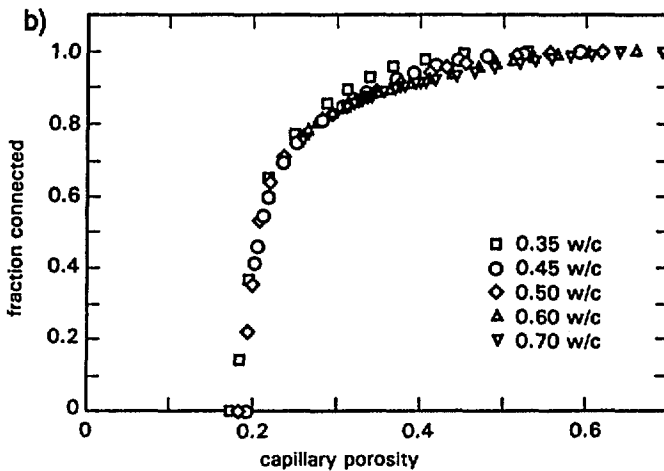


Fig. 8.3 (b).

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### **8.5.2 PORE SIZE**

During hydration, the capillary pore size, as well as the overall capillary porosity, decreases due to consumption of water during hydration, producing hydration products that fill in the capillary pore space. The size of the gel pores is fixed by the structure of the CSH, however, and so they remain constant in size. As hydration continues, the size of the capillary pores decreases down towards the roughly 10 nm gel pore size [8.2]. Therefore the importance of the pure capillary pore transport paths decreases with time due both to decreasing capillary pore size as well as to decreasing connectivity.

### **8.5.3 DIFFUSIVITY OF CEMENT PASTE**

Building on the percolation and pore size results given above, the dependence of the diffusivity and permeability of cement paste on pore structure can now be qualitatively outlined. Early in hydration the capillary pore space is fully percolated. These pores are much larger than the CSH gel pores (which are themselves also fully connected fairly early in hydration [8.6]) and so dominate the transport. As the capillary porosity decreases, the capillary pores become smaller and only partially connected, so for porosities near but above the percolation threshold, pure capillary pore paths have only slightly more influence on flow than the hybrid paths that are made up of isolated capillary pockets linked by CSH gel pores. The capillary pores are still somewhat bigger than the gel pores, but their connectivity is becoming small. Below the critical capillary porosity, all flow must now go through CSH gel pores, but flow will be dominated by paths that contain some isolated capillary pore regions, and are not just made up of pure CSH gel pores. If this were not true, then after a certain point, the diffusivity would begin going up with increasing hydration, since more CSH and thus more gel pores were being formed. This is not the case in cement paste [8.8]. The same microstructure model as was used to predict the connectivity results shown in Fig. 8.3 can also be used to compute the diffusivity of cement paste by solving Laplace's equation in the simulated pore space with a finite difference method [8.8]. Computational results confirm the above microstructural picture, and compare reasonably well with experimental measurements [8.8, 8.9].

## **8.6 Microstructure of mortar and concrete**

We now consider the effect of mortar and concrete microstructure on transport properties like ionic diffusivity and fluid permeability. For reasons of scale, mortar or concrete is considered as a composite, with the fine and

coarse aggregate being the inclusions and cement paste considered as a uniform matrix. We average out the cement paste micrometre length scale to avoid having to deal with microstructure on too wide a range of length scales at the same time. The transport properties of the aggregate are measurable and usually constant in time, while the transport properties of the cement paste depend on the original water/cement ratio, kind and quantity of admixtures, and hydration time, and to some degree on the particle size distribution. However, it will be shown below that the interfacial zone between the cement paste and aggregates may play a critical role in determining the bulk transport properties. Therefore, when averaging over the cement paste microstructure, the micrometre scale interfacial zone, which is determined from cement paste microstructure, must not be left out.

#### 8.6.1 INTERFACIAL ZONE MICROSTRUCTURE

The characteristic features seen in the interfacial zone are: (1) higher capillary porosity than in the bulk and generally bigger pores, and (2) higher CH volume fractions than are seen in the bulk. These features are typically seen in the cement paste volume that is within  $50\mu\text{m}$  of an aggregate surface [8.10].

Using the microstructure model mentioned above, we have analysed two major causes of this interfacial zone microstructure, neither of which depends on bleeding. They are: (1) the particle-packing effect, and (2) the one-sided growth effect [8.11].

The **particle-packing effect** arises from the fact that particles cannot pack together as well near a flat edge as in free space. Since the typical aggregate is many times larger than the typical cement particle, even for the fine aggregate, locally the aggregate edge appears flat to the surrounding cement particles. This inefficient packing causes less cement and higher porosity to be present initially near the aggregate surface, and so even after hydration this condition persists. The width of the interfacial zone will then be in scale with median cement particle size [8.12]. This is the main contribution to the interfacial zone microstructure, but not the only one.

The **one-sided growth effect** arises in the following way. Consider a small region of capillary pore space located out in the bulk paste part of a mortar or concrete. On the average, there is reactive growth coming into this small region from all directions, since the cement particles are originally located randomly and isotropically. Now consider a similar small region of capillary pore space, but located very near an aggregate surface. Reactive growth is coming into this region from the cement side, but not from the aggregate side [8.11].

Mineral admixtures like silica fume and fly ash can also be incorporated into the model, and their effect on interfacial zone properties



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simulated [8.13]. We have found that the two main variables of importance for mineral admixtures are particle size and reactivity with calcium hydroxide. The size of the mineral admixture controls the width of the packing effect at the aggregate edge, with smaller admixtures allowing better packing nearer to the aggregate edge. The reactivity controls how much calcium hydroxide can be consumed, and converted to CSH. Assuming adequate dispersion, we have found, using the model, that the effectiveness of a mineral admixture in improving the interfacial zone microstructure increases as its reactivity increases and its size decreases [8.13].

Properties of the aggregate can be studied as well, such as the effect of porous and/or reactive aggregates on the interfacial zone microstructure [8.12]. We have found it possible to explain the influence of each of these materials variables on the interfacial zone microstructure in terms of the particle-packing effect and the one-sided growth effect. These ideas then serve as a useful theoretical framework to unify analysis of how material variables affect interfacial zone microstructure [8.12].

### 8.6.2 CONCRETE CONSIDERED AS A COMPOSITE MATERIAL

If we were to make a concrete out of cement paste and zero porosity aggregate, with no interfacial zones present, then the ionic diffusivity and fluid permeability of the concrete would rigorously have to be lower than the corresponding values for the cement paste. This is because the aggregates, assumed to be fully dense, would have zero transport coefficients, so that the mixture must have lower bulk properties. For this kind of composite, the bulk values of transport coefficients are always less than a simple volume average of the individual phase properties, owing to the random geometry and the nature of the equations that define the various properties, and only decrease as more of the second phase (aggregate) is added. Useful bounds have been derived for the effective bulk properties in terms of the properties of the constituents [8.14].

There are not enough good data in the literature to carefully study the transport properties of concrete using composite theory, which requires simultaneous measurement of the cement paste host and concrete transport properties while the aggregate volume fraction is systematically varied. There is some such careful work, however, on the elastic moduli of mortar [8.15, 8.16]. Some recent work does show that the effective transport properties of concrete can increase greatly as more aggregate is added past a critical amount [8.17]. There are also data showing that concrete can have up to 100 times the water permeability of the cement paste it is made from [8.2]. The only possible microstructural explanation of this behaviour, besides that of extensive microcracking, is the effect of

transport of fluid or ions through the interfacial zones. It is already known that the interfacial zone regions contain pores larger than those in the bulk paste. However, if the interfacial zones do not percolate, then their effect on transport will only be negligible, as any transport path through the concrete would have to go through the bulk cement paste. Transport properties would then be dominated by the bulk cement paste transport properties.

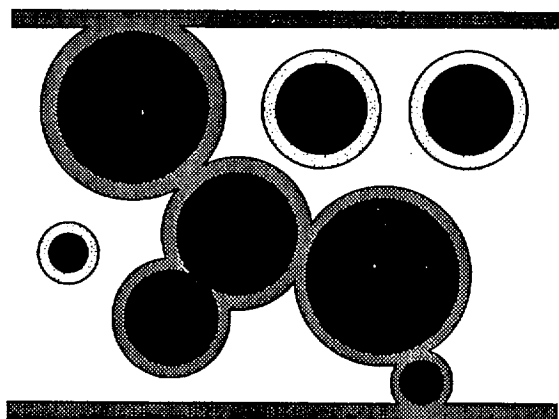
### 8.6.3 INTERFACIAL ZONE PERCOLATION

To study the percolation or connectivity of the interfacial zones in concrete is not simple, as the geometry of this phase is complex. Fortunately, in the percolation literature there is a model that is almost perfectly suited for this study: the **hard core/soft shell** model [8.18].

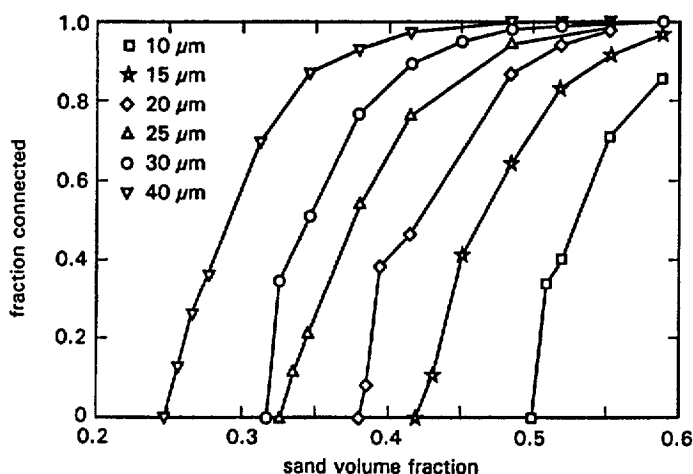
This model starts with a random suspension of 'hard' spherical particles, which are 'hard' in the sense that they are packed without being allowed to overlap, as in a suspension. Then concentric spherical shells are placed around each particle, where the spherical shells all have the same thickness, and are allowed to overlap freely. The volume fraction of shells required to make the shells percolate, which is when a continuous soft shell pathway first becomes established, is then computed. The volume fraction of soft shells required for percolation is a function of how many hard core particles are present, and the thickness of the soft shell. Obviously when more hard core particles are packed in a given volume, there is less space between them, so thinner soft shells will be able to percolate. When there are fewer hard core particles present, thicker shells will be required for percolation of the shell phase. Figure 8.4 shows a schematic drawing of the basic concept of a two-dimensional version of this model.

To study interfacial zone percolation in concrete, we take a fixed shell thickness to represent the interfacial zone, and pack spherical aggregate particles that are then surrounded by these shells. The width of the interfacial zone should be independent of aggregate size, as long as the median aggregate size is at least 5–10 times the median cement particle size [8.12]. The size distribution of the hard core particles is taken from measured aggregate size distributions [8.19–8.21]. The fraction of the total shell volume that forms part of a connected cluster is then computed as a function of the volume fraction of aggregate present.

Results for a mortar are shown in Fig. 8.5, in which each curve shows the connectivity of the interfacial zones for different choices of interfacial zone thickness. When comparing against Portland cement mortar mercury intrusion data [8.19–8.21], it was found that a choice of 20  $\mu\text{m}$  for the interfacial zone thickness gave the best agreement with the mercury data. The mercury data gave an idea of what the percolation threshold of the interfacial zones was by showing a large increase in large pores intruded



**Fig. 8.4.** Schematic two-dimensional picture of the percolation of the interfacial zones (grey) around aggregates (black). The darker grey interfacial zones form a percolated cluster.



**Fig. 8.5.** Showing the fraction of the total interfacial zone volume that is a part of a percolated (continuous) cluster as a function of aggregate volume fraction and for several interfacial zone thicknesses.

at the mercury breakthrough point [8.22] at a certain aggregate volume fraction. The width given in scanning electron microscope studies of the interfacial zone, 30–50  $\mu\text{m}$ , is defined by measuring from the aggregate edge to where the measured porosity assumes its bulk value. This would not be the width seen by mercury porosimetry, because it is probable that the larger pores will be found in the larger-porosity region nearer to the aggregate, which will be seen first by the mercury. Also, as to effect on

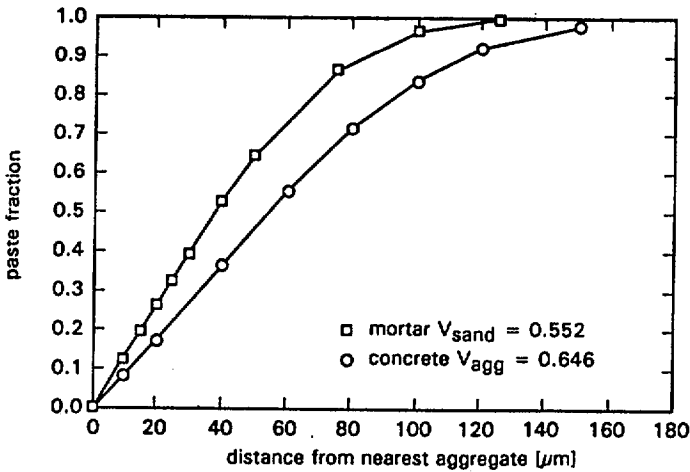


Fig. 8.6. Showing the fraction of the total cement paste volume fraction that lies within a given distance from an aggregate surface, for a mortar with a sand volume fraction of 0.552, and a concrete with an aggregate volume fraction of 0.646.

transport properties, the inner region of the interfacial zone is of more importance, since its transport properties will be higher than the outer region because of the larger pore size and porosity. The width of 20  $\mu\text{m}$  given by the hard core/soft shell model is an effective width, where this width contains the larger pores that would be important for transport. Figure 8.5 also shows that for an aggregate volume fraction of 40% or more and an interfacial zone thickness of at least 20  $\mu\text{m}$ , the interfacial zones will be percolated at least partially, and will be fully percolated for aggregate volume fractions greater than 50%. Most concretes have aggregate volume fractions well above 50%, so that, in general, we can conclude that the interfacial zones in usual Portland cement concrete are percolated, and so will have an effect on transport properties. To calculate the size of this effect requires more work. The fraction of the cement paste that lies in interfacial zones can be calculated with the hard core/soft shell model for a given aggregate volume fraction and particle size distribution. Results are given in Fig. 8.6 for a specific mortar and concrete [8.19]. Figure 8.6 shows that quite a large part of the cement paste matrix lies within an interfacial zone, with about 20% lying within 20  $\mu\text{m}$ , and about 50% lying within 50  $\mu\text{m}$  of an aggregate surface.

## 8.7 Critically needed future work

In order to further understand the relationships between concrete microstructure and transport properties, more experimental measurements of

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transport properties must be done on well-characterized samples. To check carefully whether a given analytical theory is useful, or if a computer simulation computation of a transport property is correct, the concrete sample must have the following known quantities: (1) degree of hydration and porosity of the cement paste, (2) the volume and size distribution of aggregates, (3) the width of the interfacial zones, and most importantly, (4) the values of the transport coefficients of interest measured separately for the matrix and aggregate materials.

On the theoretical side, more sophisticated effective medium or homogenization theories need to be developed. It is possible that such effective medium theories, even if made more sophisticated, can never work well on cement-based materials, but the attempt should be made. There is a body of knowledge from homogenization theory and composite materials science that has not been taken advantage of for cement-based materials [8.23]. The simple Maxwell-type theories [8.24] are not enough, since they do not take into account the complexities of cement paste microstructure, nor, when applied to concrete considered as a composite, do they take into account the interfacial zones. More and better fundamental computer simulations [8.25] need to be carried out as well, in order to make microstructure property connections through comparing digital images of microstructure with computed properties. It is also possible that ideas currently being developed in other areas of materials science for **interpenetrating phase composites (IPCs)** will be useful for cement-based materials [8.26]. IPCs have more than one continuous phase, which form interpenetrating networks. Since both the interfacial zones and the bulk cement paste are percolated in concrete, concrete must be considered to be an IPC.

## 8.8 Conclusions and summary

It has been shown that theoretical understanding of the microstructure transport property relationships of concrete, from the cement paste up to the full composite, can be based on the basic ideas of pore size and connectivity, with connectivity defined rigorously using percolation concepts. These concepts give a fairly complete, although at present mainly qualitative, picture of how transport properties depend on microstructure in concrete. These ideas have already been tested for cement paste and found to be valid. The concept of interfacial zone percolation in concrete needs to be tested, and its effect on transport carefully quantified. Careful materials science experiments, in conjunction with computer simulation computations and new effective medium theories that are based on IPC concepts, can help validate this theoretical understanding of the microstructure-transport property relationships of concrete.

## 8.9 References

- 8.1. Allen, A.J., Oberthur, R.C., Pearsons, D., Schofield, P. and Wilding, C.R. (1987) Development of the fine porosity and gel structure of hydrating cement systems. *Philosophical Magazine B*, Vol. 56, No. 3, pp. 263-288.
- 8.2. Young, J.F. (1988) A review of the pore structure of cement paste and concrete and its influence on permeability, in *Permeability of Concrete*, eds D. Whiting and A. Walitt, ACI SP-108, American Concrete Institute, Detroit.
- 8.3. Garboczi, E.J., Thorpe, M.F., DeVries, M. and Day, A.R. (1991) Universal conductivity curve for a plane containing random holes. *Physical Review A*, Vol. 43, pp. 64-73.
- 8.4. Garboczi, E.J. (1990) Permeability, diffusivity, and microstructural parameters: a critical review. *Cement and Concrete Research*, Vol. 20, pp. 591-601.
- 8.5. Chen, Y. and Odler, I. (1992) On the origin of Portland cement setting. *Cement and Concrete Research*, Vol. 22, pp. 1130-1140.
- 8.6. Bentz, D.P. and Garboczi, E.J. (1991) Percolation of phases in a three-dimensional cement paste microstructural model. *Cement and Concrete Research*, Vol. 21, pp. 325-344.
- 8.7. Powers, T.C., Copeland, L.E. and Mann, H.M. (1959) Capillary continuity or discontinuity in cement pastes. *Journal of the Portland Cement Association, Research and Development Laboratories*, Vol. 1, No. 2, May, pp. 38-48.
- 8.8. Garboczi, E.J. and Bentz, D.P. (1992) Computer simulation of the diffusivity of cement-based materials. *Journal of Materials Science*, Vol. 27, pp. 208-392.
- 8.9. Christensen, B.J., Mason, T.O., Jennings, H.M., Bentz, D.P. and Garboczi, E.J. (1992) Experimental and computer simulation results for the electrical conductivity of Portland cement paste, in *Advanced Cementitious Systems: Mechanisms and Properties*, ed. F.P. Glasser, G.J. McCarthy, J.F. Young, T.O. Mason, and P.L. Pratt, Materials Research Society, Pittsburgh.
- 8.10. Scrivener, K.L. (1990) The microstructure of concrete, in *Materials Science of Concrete I*, ed. J. Skalny, American Ceramic Society, Westerville.
- 8.11. Garboczi E.J. and Bentz, D.P. (1991) Digital simulation of the aggregate paste interfacial zone in concrete. *Journal of Materials Research*, Vol. 6, No. 1, pp. 196-201.
- 8.12. Bentz, D.P., Garboczi, E.J. and Stutzman, P.E. (1992) Computer modelling of the interfacial zone in concrete, in *Interfaces in Cementitious Composites*, ed. J.C. Maso, E & FN Spon, London, pp. 107-116.
- 8.13. Bentz D.P. and Garboczi, E.J. (1991) Simulation studies of the effects of mineral admixtures on the cement paste aggregate interfacial zone. *ACI Materials Journal*, Vol. 88, No. 5, pp. 518-529.
- 8.14. Hashin, Z. (1983) Analysis of composite materials: a survey. *Journal of Applied Mechanics*, Vol. 50, pp. 481-505.
- 8.15. Zimmerman, R.W., King, M.S. and Monteiro, P.J.M. (1986) *Cement and Concrete Research*, Vol. 16, pp. 239 ff.
- 8.16. Ulrik Nilsen A. and Monteiro, P.J.M. (1993) Concrete: a three phase material. *Cement and Concrete Research*, Vol. 23, pp. 147-151.
- 8.17. Houst, Y.F., Sadouki, H. and Wittmann, F.H. (1992) Influence of aggregate concentration on the diffusion of CO<sub>2</sub> and O<sub>2</sub>, in *Interfaces in Cementitious Composites*, ed. J.C. Maso, E & FN Spon, London, pp. 279-288.

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- 8.18. Torquato, S. (1986) *J. Chem. Phys.*, Vol. 85, pp. 624–628.
- 8.19. Winslow, D.N., Cohen, M., Bentz, D.P., Snyder, K.A. and Garboczi, E.J. Percolation and porosity in mortars and concretes. *Cement and Concrete Research*, in press.
- 8.20. Snyder, K.A., Winslow, D.N., Bentz, D.P. and Garboczi, E.J. (1992) Effects of interfacial zone percolation on cement-based composite transport properties, in *Advanced Cementitious Systems: Mechanisms and Properties*, ed. F.P. Glasser, G.J. McCarthy, J.F. Young, T.O. Mason, and P.L. Pratt, Materials Research Society, Pittsburgh, pp. 265–270.
- 8.21. Snyder, K.A., Bentz, D.P., Garboczi, E.J. and Winslow, D.N. (1992) Interfacial zone percolation in cement–aggregate composites, in *Interfaces in Cementitious Composites*, ed. J.C. Maso, E & FN Spon, London, pp. 259–268.
- 8.22. Winslow D.N. and S. Diamond, S. (1970) *ASTM Journal of Materials*, Vol. 5, p. 564.
- 8.23. McLachan, D.S., Blaszkiewicz, M. and Newnham, R.E. (1990) *Journal of the American Ceramic Society*, Vol. 73, pp. 2187 ff.
- 8.24. Ross MacDonald, J. (1987) *Impedance Spectroscopy: Emphasizing Solid Materials and Systems*, John Wiley and Sons, New York.
- 8.25. Garboczi E.J. and Bentz, D.P. (1990) *Materials Science of Concrete Vol. II*, ed. J.P. Skalny, Ed., American Ceramic Society, Westerville.
- 8.26. Clarke, David R. (1992) Interpenetrating phase composites. *Journal of the American Ceramic Society*, Vol. 75, pp. 739–759.